

COMPARISON OF MICROWAVE-ASSISTED CHEMICALS IN
DEMULSIFICATION OF WATER-IN-CRUDE OIL EMULSIONS

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Report submitted in partial fulfillment of the requirements for the award of the
Degree of Bachelor of Chemical Engineering (Chemical)

Faculty of Chemical and Natural Resources Engineering

UNIVERSITI MALAYSIA PAHANG

JANUARY 2012

ABSTRACT

Demulsification (emulsion breaking or emulsions destabilizing) is important in many industry applications such as the petroleum industry, painting and waste-water treatment in environmental technology. Chemical and microwave heating demulsification is the most widely used method of demulsifying the water-in-crude oil emulsions and both methods accelerate the emulsion destabilizing process. This research combined the chemical with microwave-assisted to increase the efficiency of demulsification and reduce the chemical usage to prevent any environmental issues. The effect of chemical demulsification with microwave-assisted operations on the stability and properties of water-in-crude oil emulsions was assessed experimentally by using different types of demulsifiers which are Amine and Polymeric demulsifiers with microwave heating. By using the sample of water-in-crude oil emulsions which prepared by adding artificial emulsifiers (Span 83) which had formed the most stable emulsion after the complete screening of stability part was conducted, the chemical demulsifiers were added in the emulsions to break the emulsion with the assistant of microwave heating to increase the performance. The research found that Hexylamine and Cocoamine had the high efficiency of the demulsification with the assistant of microwave heating which was different from the conventional method but the latter was better as it was more environmental friendly. Overall results show that demulsification by microwave heating was faster as compared to the gravity sedimentation and it does not require much chemical additions to boost the breaking of the emulsion.

ABSTRAK

Demulsifikasi (pemecahan emulsi atau pentidakstabilan emulsi) adalah penting dalam banyak aplikasi industri, misalnya industri petroleum, lukisan dan rawatan air sisa dalam teknologi alam sekitar. Demulsifikasi dengan menggunakan kimia dan pemanasan dengan gelombang mikro adalah kaedah yang digunakan secara meluas dalam memecahkan emulsi air dalam minyak mentah dan kedua-dua kaedah ini dapat mempercepatkan proses pentidakstabilan emulsi. Kajian ini menggabungkan bahan kimia dengan pembantuan pemanasan gelombang mikro untuk meningkatkan kecekapan demulsifikasi dan mengurangkan penggunaan bahan kimia untuk mengurangkan mana-mana isu alam sekitar. Kesan operasi demulsifikasi kimia dengan bantuan gelombang mikro terhadap kestabilan dan sifat-sifat emulsi air dalam minyak mentah telah dinilai melalui uji kaji dengan menggunakan pelbagai jenis pendemulsi seperti pendemulsi Amine dan polimer dengan bantuan pemanasan gelombang mikro. Dengan menggunakan sampel emulsi air dalam minyak mentah yang disediakan dengan menambahkan pengemulsi tiruan atau buatan (SPAN 83) dimana ia membentuk emulsi yang paling stabil selepas proses pemerhatian lengkap dijalankan terhadap kestabilan emulsi. Selepas itu, pendemulsi kimia ditambah dalam emulsi untuk memecahkan emulsi dengan pembantuan pemanasan gelombang mikro untuk meningkatkan prestasi. Penyelidikan mendapati bahawa demulsifikasi kimia dengan pembantuan pemanasan gelombang mikro dengan menggunakan pendemulsifi Hexylamine dan Cocoamine mempunyai kecekapan yang paling tinggi dimana ia berbeza dari kaedah konvensional tetapi Cocoamine adalah lebih baik kerana ia adalah lebih mesra alam sekitar. Keputusan secara keseluruhan menunjukkan bahawa demulsifikasi kimia dengan bantuan pemanasan gelombang mikro adalah lebih cepat berbanding dengan pemendapan graviti dan tambahan lagi ia tidak memerlukan penambahan bahan kimia yang banyak untuk meningkatkan prestasi pemecahan emulsi.

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LIST OF SYMBOLS

HLB	-	Hydrophile-Lipophile Balance
Σ	-	Summation
$\epsilon'_{r,w}$	-	Dielectric constant of water
$\epsilon''_{r,w}$	-	Dielectric loss of water
$\epsilon'_{r,o}$	-	Dielectric constant of crude oil
$\tan \delta_o$	-	Loss tangent of crude oil
$q_{MW,z}$	-	The volume rate of heat generation
$P_{(z)}$	-	Local time-average microwave power flux at the surface of container (watts/cm ²)
m	-	Mass (g) of the sample
A	-	Sample container's area
$P_{(0)}$	-	Microwave power flux at z=0 (watts/cm ²)
α_E	-	Attenuation factor
f_o	-	Frequency of incident microwave
c	-	Electromagnetic wave velocity = speed of light
z	-	Pathlength (R-r)
R	-	Radius of sample container, cm
r	-	Radial coordinate, cm
$q_{MW,(n)}$	-	The volume rate of heat generation by the n-th forward and reflected passes
nR^2H	-	The volume of irradiated emulsion.
H	-	Height of container, cm

h	-	Convective heat transfer coefficient, $\text{cal/s.cm}^2.\text{°C}$
A	-	Convective heat transfer area, cm^2
V	-	Volume of irradiated emulsion, cm^3
T_m	-	Temperature of emulsion, °C
T_a	-	Ambient Temperature, °C
ε	-	emissivity of surface
σ	-	Stefan-Boltzmann constant= $5.672 \times 10^{-8} \text{ W/m}^2.\text{K}^4$
ρ	-	Density of emulsion, g/cm^3
C_p	-	Heat capacity at constant pressure, cal/g.°C
$\frac{dT}{dt}$	-	Rate of temperature increase in °C/s
ρ_m	-	Density of emulsion, g/cm^3
ρ_w	-	Density of water, g/cm^3
ρ_o	-	Density of crude oil, g/cm^3
$C_{p,m}$	-	Heat capacity of emulsion, cal/g.°C
$C_{p,w}$	-	Heat capacity of water, cal/g.°C
$C_{p,o}$	-	Heat capacity of crude oil, cal/g.°C
Φ	-	Volume fraction of emulsified water
D_p	-	Penetration depth, within a sample for a
λ_m	-	Wavelength
q_{MW}	-	Average volume rate of heat generation induced by microwaves, cal/s.cm^3
$q_{MW,w}$	-	Water volume rate of heat generation induced by microwaves, cal/s.cm^3
$q_{MW,o}$	-	Crude oil volume rate of heat generation induced

		by microwaves, cal/s.cm ³
% water separation	-	Percentage of water separation
V	-	Volume of water layer (mL)
V ₀	-	Original amount of water (mL)
v	-	Settling velocity of the water droplets
D	-	Diameter of droplets
G	-	Acceleration caused by of gravity
μ	-	Oil viscosity

LIST OF ABBREVIATIONS

w/o	-	water-in-crude oil
o/w	-	crude oil-in-water
w/o/w	-	water-in-crude oil-in-water
DC	-	Direct Current
AC	-	Alternating Current
Triton-X-100	-	Octyl phenol ethoxylate
Span 80/83	-	Sorbitan monooleate
Tween 20/80	-	Polyorbates
SDDS	-	Sodium Dodecyl Sulfide
Cocamide DEA	-	Cocamide Diethanolamine
BS&W	-	Basic Sediment and Water
HLB	-	Hydrophile-Lipophile Balance
H/C	-	Hydrogen/Carbon
AFM	-	Atomic Force Microscopy
PIT	-	Phase Inversion Temperature
PEG-600	-	Polyethylene glycol 600

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

From the era of globalization, the demands of crude oil in the world increases sharply but the resources are limited. In addition, the crude oil obtained from deep sea is normally emulsified with the water which decreases the quality and quantity of the crude oil in the process. Crude oil is composed of mostly hydrocarbons, both aliphatic and aromatic, as well as some molecules that naturally occurring surfactants in crude oil (asphaltens and resins) have been identified as largely responsible for the stability of these emulsions. An emulsion may be tight (difficult to break) or loose (easy to break), whether an emulsion is tight or loose depends on a number of factors such as the percentages of oil and water found in the emulsion, the amount of agitation, the types and amounts of emulsifying agents present, as well as the properties of oil and water (Ali and Algam, 2000) **(in Abdurahman and Rosli, 2006)**

Demulsification is introduced which is to break the emulsion water-in-crude oil (w/o). Demulsification is very essential industrial process which is to remove the water in the crude oil which to improve the quality and quantity of the crude oil that need to be commercialized. There are many techniques which have been used as to demulsify the water-in-crude oil emulsions. For instances, chemical demulsifier, microwave heating, electrostatic demulsification, centrifugation technique, sedimentation technique and many on.

Based on the previous research, chemical demulsifier is the widely used method to demulsify the emulsion and the efficiency is considered quite high. Moreover, chemical demulsifier is easier to obtain but it will create another environmental issues. The w/o emulsions is normally has low Hydrophile-Lipophile Balance (HLB) number which has high affinity to the oil or it can be refer as lipophilic or hydrophobic. Hence, water soluble chemical demulsifiers are frequently used to demulsify the w/o emulsions. These emulsion are moderate (2000-50,000) molecular weight, polydispersed interfacially active polymers. The method of production of oil soluble demulsifiers in most cases involves handling of dangerous chemicals like ethylene and propylene oxide. It would be highly desirable to have demulsifier that are water soluble but as effective as their oil soluble counterpart (Bhattacharyya, 1992) with the ability to reduce the environment problems.

Furthermore, microwave heating also another technique that is widely used and it comes out as alternative to solve for the chemical demulsifier's environmental issues. Microwave heating is more economical and the device is available and is easily obtained. Besides, the procedures are users friendly and heating is more rapidly and uniformly (Abdurahman, Rosli, and Azhary, 2010) compares with conventional heating. The theory of microwave demulsification was first introduced by Klaila (1983) and Wolf (1986) in their patent applications. Chih and Yeong (2002), Fang *et al.* (1989) and Fang and Lai (1995) reported demulsification of w/o emulsions by microwave radiation. **(in Abdurahman, Rosli and Anwaruddin, 2006)**

1.2 SIGNIFICANCE OF THE STUDY

The world nowadays concern is to save planet from any pollution, therefore in the application of chemical with microwave-assisted, the environmental problems can be decreased in a significant way as in this method, the usage of pure chemical is reduced with the help of microwave and at the same time it can maximize the efficiency. In addition, the pure chemical used is designed or planned to be environmental friendly,